

Investigation of Li Diffusion and Transference Numbers of Ionic Liquid Based Electrolytes by ^7Li NMR

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We investigated the conductivity of different ionic-liquid based electrolytes together with the Li ion diffusion coefficients determined from field gradient nuclear magnetic resonance spectroscopy. Five different systems were chosen which cover a broad range of conductivities as well as Li ion diffusion coefficients. 1M LiPF_6 in EC/DMC (1:1 wt%) is a standard electrolyte used in Li-ion batteries and 0.01M LiCl in H_2O was used as reference system with known ionic conductivity (0.11 S/m) and known diffusion coefficient ($1.03 \cdot 10^{-9} \text{ m}^2/\text{s}$) at 298 K. Further systems in this study were 0.3M Li-TFSI in MPPyr-TFSI, 0.5M Li-TFSI in MPPyr-TFSI/EC (7:3 wt%) and 1.3M Li-TFSI in DMMA-TFSI/PC (1:1 wt%) which consist of Li salts dissolved in mixtures of an ionic liquid and an organic solvent. The highest conductivity over the whole temperature range is obtained for 1M LiPF_6 in EC/DMC while the lowest conductivity is observed for 0.01M LiCl in H_2O , caused by the small concentration of Li ions. All systems could be described by an Arrhenius-type behavior with activation energies between 0.16 eV and 0.33 eV. DOSY NMR measurements give diffusion coefficients in the range from $6 \cdot 10^{-12}$ to $10^{-9} \text{ m}^2/\text{s}$. From this, transference numbers ranging from 0.76 for 1M LiPF_6 in EC/DMC to 0.02 for 0.3M Li-TFSI in MPPyr-TFSI were derived. These explain the poor performance of 0.3M Li-TFSI in MPP-TFSI in the Li batteries in contrast to 1.3M Li-TFSI in DMMA-TFSI/PC which has an even slightly smaller overall conductivity and still shows reasonable performance in the batteries.

Electrochemical investigation

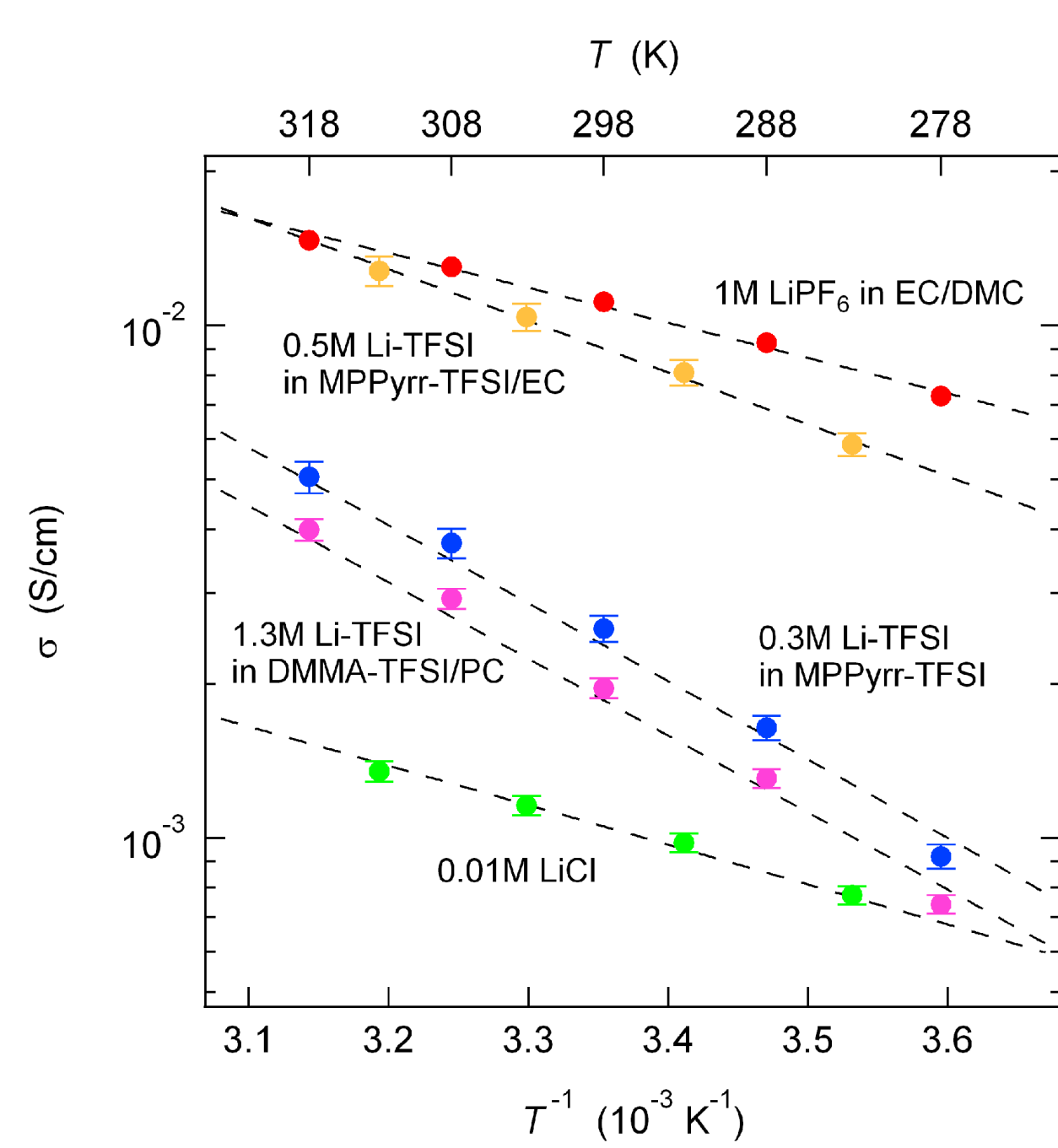


Fig. 1: Conductivity of the different electrolytes.

- $E_A \approx 0.17 \text{ eV}$ activation energies for 0.01M LiCl in H_2O and 1M LiPF_6 in EC/DMC (hints at fast diffusion of the charge carriers.)
- The other electrolytes show activation energies of $E_A \approx 0.33 \text{ eV}$

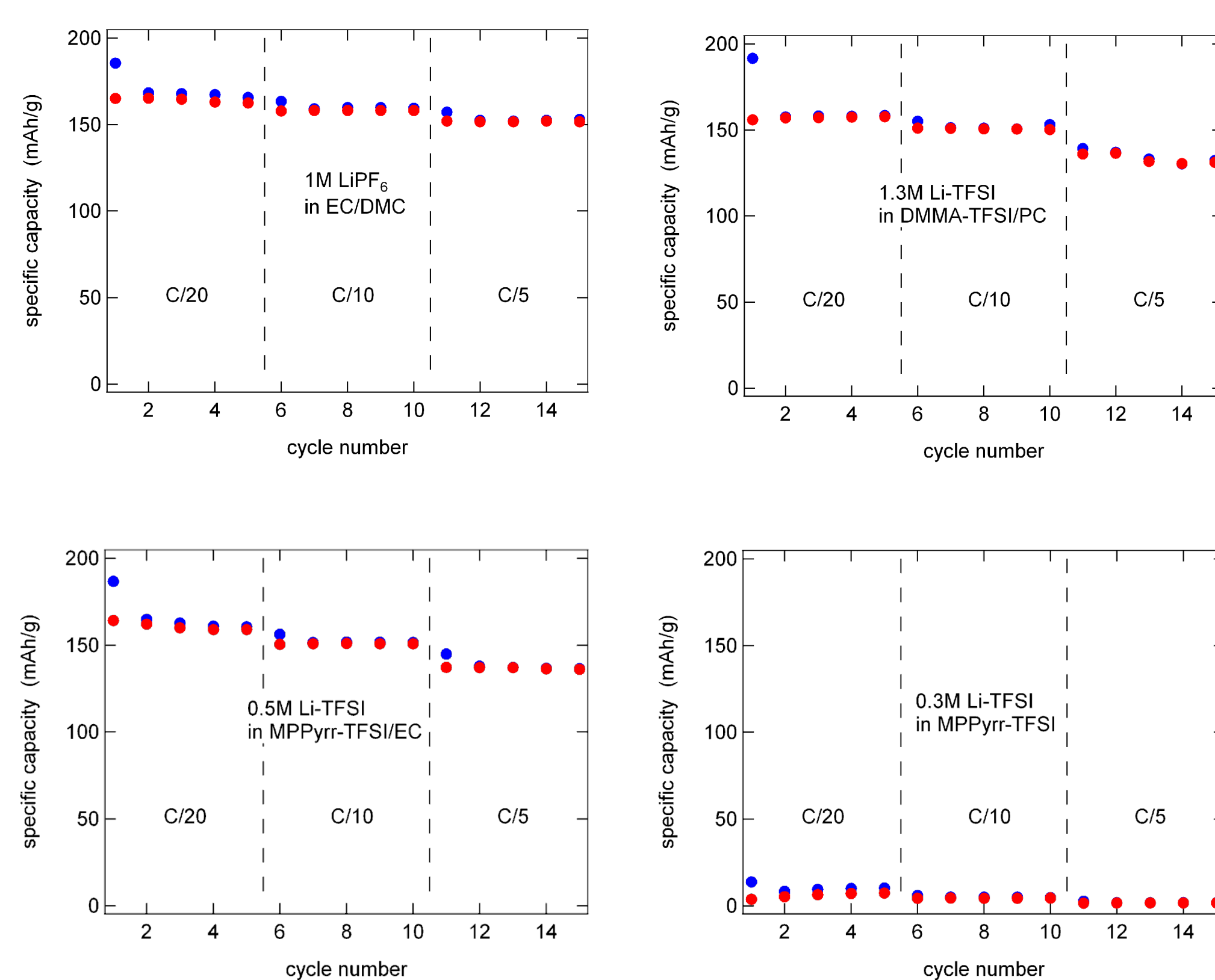


Fig. 2 a)-d): Specific charge (blue) and discharge (red) capacities for different electrolytes for galvanostatic cycling with rates of C/20, C/10, and C/5.

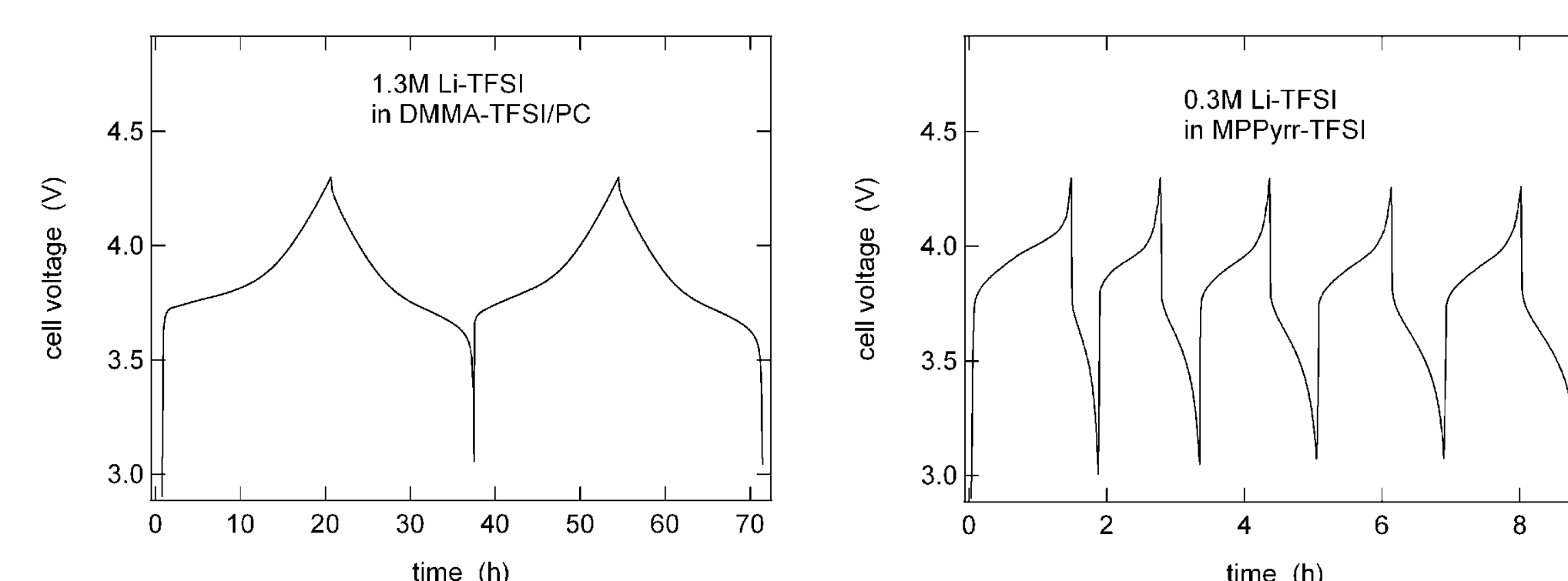


Fig. 3 a) and b): Voltage profile for galvanostatic cycling with a rate of C/20 for a) 1.3M Li-TFSI in DMMA-TFSI/PC and b) 0.3M Li-TFSI in MPPyr-TFSI.

- The different ionic-liquid based electrolytes and 1M LiPF_6 in EC/DMC were tested in Li batteries with $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ as positive electrode and Li metal as negative electrode (Fig. 2 and Fig 3)
- 1M LiPF_6 in EC/DMC shows the best cycling performance.
- The electrolytes containing ionic liquids as well as organic solvents still shows reasonable cycling performance with discharge capacities of more than 150 mAh/g for C/20 rate
- For 0.3M Li-TFSI in MPPyr-TFSI the specific capacities are extremely small with values of 3-7 mAh/g although the conductivity is even slightly higher than that of 1.3M Li-TFSI in DMMA-TFSI/PC
- In Fig. 3 a) 1.3M Li-TFSI in DMMA-TFSI/PC shows clearly the well-known plateau at voltages between 3.7 and 4.2 V with a length close to 20h. For 0.3M Li-TFSI in MPPyr-TFSI in Fig 3 b) this plateau is hardly visible

^7Li DOSY NMR

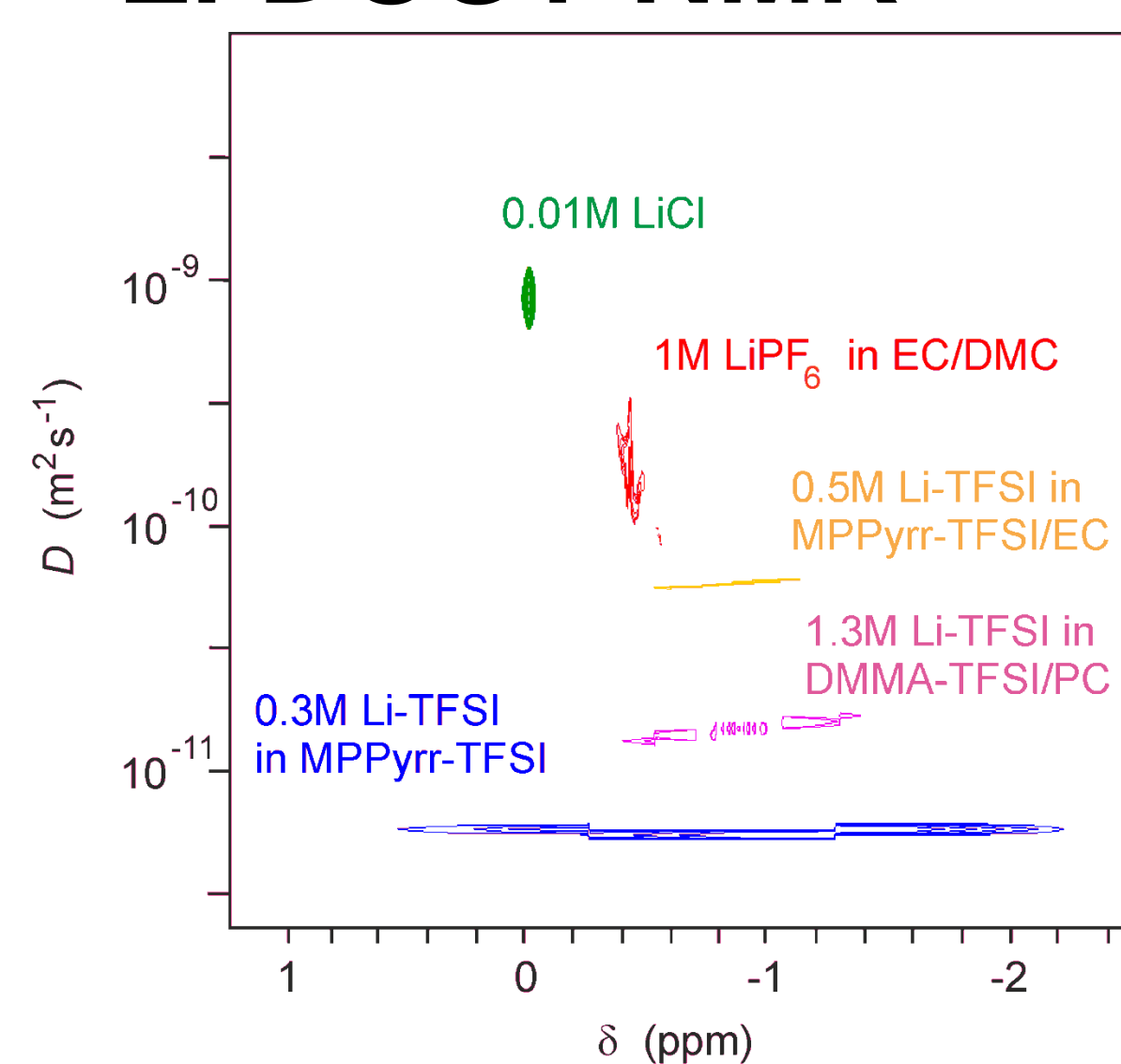


Fig. 4: ^7Li DOSY NMR spectra of different electrolytes.

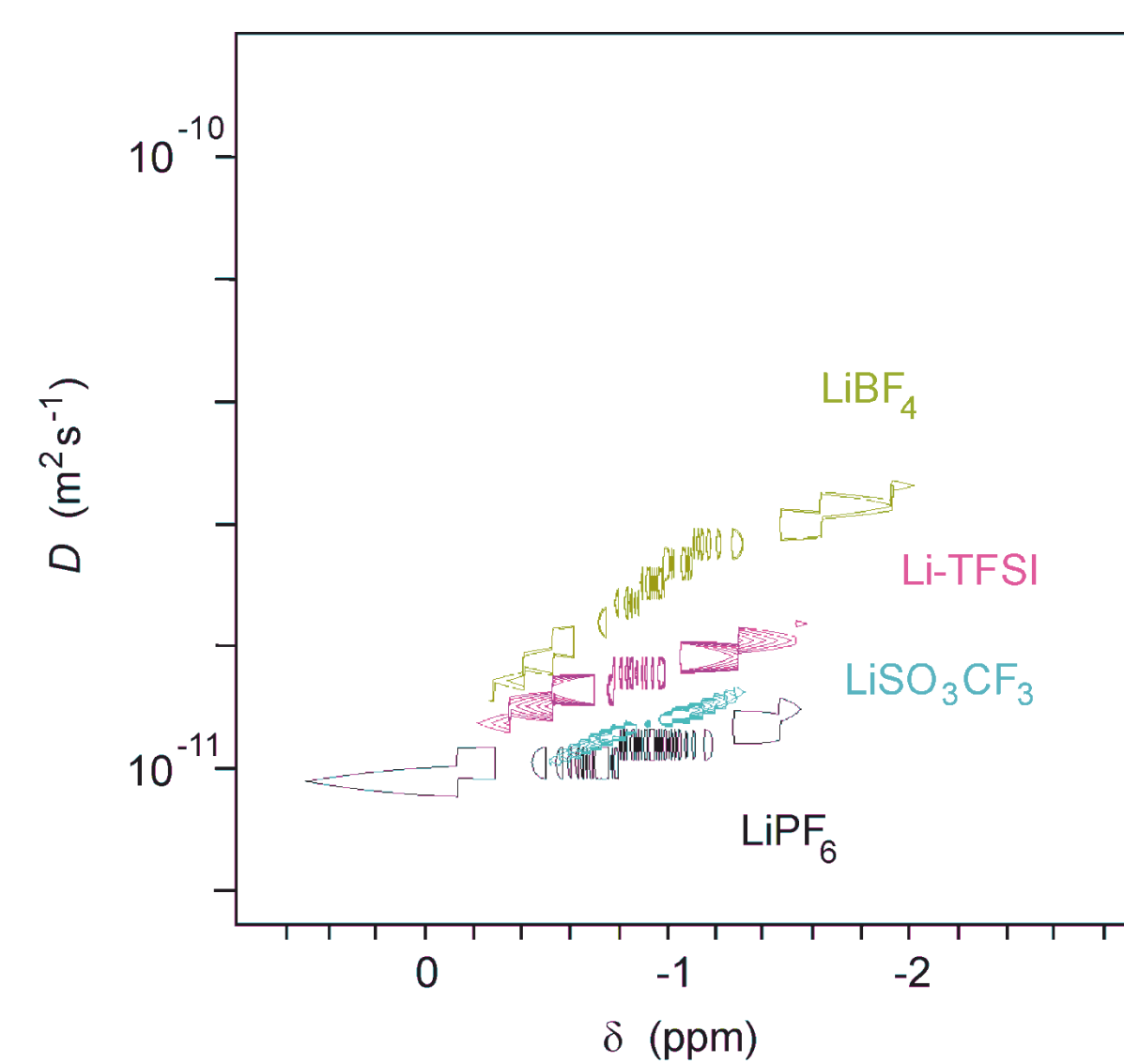


Fig. 5: ^7Li DOSY NMR spectra of electrolytes consisting of the given salts dissolved in DMMA-TFSI/PC.

electrolyte	σ in S/m	E_A in eV	D in m^2/s	t_{Li}
0.01M LiCl in H_2O	0.11 ± 0.02	0.18 ± 0.01	$(1.03 \pm 0.01) \cdot 10^{-9}$	0.36 ± 0.06
1M LiPF_6 in EC/DMC	1.11 ± 0.10	0.16 ± 0.02	$(2.24 \pm 0.03) \cdot 10^{-10}$	0.76 ± 0.07
0.5M Li-TFSI in MPPyr-TFSI/EC	0.93 ± 0.05	0.22 ± 0.02	$(5.72 \pm 0.98) \cdot 10^{-11}$	0.12 ± 0.02
1.3M Li-TFSI in DMMA-TFSI/PC	0.20 ± 0.01	0.32 ± 0.01	$(1.46 \pm 0.03) \cdot 10^{-11}$	0.30 ± 0.02
0.3M Li-TFSI in MPPyr-TFSI	0.26 ± 0.02	0.33 ± 0.01	$(5.88 \pm 0.04) \cdot 10^{-12}$	0.02 ± 0.01

electrolyte	σ in S/m	D in m^2/s	t_{Li}
1.3M LiPF_6 in DMMA-TFSI/PC	0.25 ± 0.02	$(1.11 \pm 0.03) \cdot 10^{-11}$	0.22 ± 0.02
1.3M LiSO_3CF_3 in DMMA-TFSI/PC	0.23 ± 0.03	$(1.25 \pm 0.02) \cdot 10^{-11}$	0.27 ± 0.04
1.3M Li-TFSI in DMMA-TFSI/PC	0.20 ± 0.01	$(1.46 \pm 0.03) \cdot 10^{-11}$	0.30 ± 0.03
1.3M LiBF_4 in DMMA-TFSI/PC	0.41 ± 0.04	$(2.13 \pm 0.03) \cdot 10^{-11}$	0.25 ± 0.02

- Range of diffusion coefficients covered by the different electrolytes is larger than two orders of magnitude (Fig 4)
- Largest Li diffusion coefficient is obtained for 0.01M LiCl in H_2O with a value of $D=1.03 \cdot 10^{-9} \text{ m}^2/\text{s}$ at 298 K (A. Aouzerat-Elarby et al.)
- Second fastest diffusion is observed for 1M LiPF_6 in EC/DMC ($D=2.24 \cdot 10^{-10} \text{ m}^2/\text{s}$)
- 0.5M Li-TFSI in MPPyr-TFSI/EC ($D=5.72 \cdot 10^{-11} \text{ m}^2/\text{s}$), 1.3M Li-TFSI in DMMA-TFSI/PC ($D=1.46 \cdot 10^{-11} \text{ m}^2/\text{s}$) and 0.3M Li-TFSI in MPPyr-TFSI ($D=5.88 \cdot 10^{-12} \text{ m}^2/\text{s}$) show much slower diffusion processes of the Li ions
- Changes of line width in the frequency domain reflect the trend from a quasi-static environment with a broad distribution of local Li environments to a motionally averaged environment
- Transference numbers determined by this method show a strong variation ranging from 0.76 for 1M LiPF_6 in EC/DMC to 0.02 for 0.3M Li-TFSI in MPPyr-TFSI
- Very low transference number in the latter case explains the poor performance in the Li batteries
- Diffusion coefficients obtained from DOSY NMR allow the explanation of the poor performance of 0.3M Li-TFSI in MPPyr-TFSI in the Li batteries in contrast to 1.3M Li-TFSI in DMMA-TFSI/PC
- Diffusion coefficient is strongly influenced by the cation of the ionic liquid but also by the addition of organic solvents
- Anion of the Li salt has only weak influence on the Li diffusion and transference numbers of 0.26 ± 0.04 are obtained for all Li salts (Fig. 5)

Summary

Li diffusivities and the transference numbers of the Li ions reveal large differences in the cycling performance during galvanostatic cycling in Li battery cells although the different electrolytes show very similar conductivities

- The addition of organic solvents to the ionic liquids clearly enhances these transference numbers while the choice of the lithium salt has only a weak influence